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(54) Title: USE OF PERCARBAMIC ACIDS AND DIACYL PERCARBAMATES AND PRECURSORS THEREFOR

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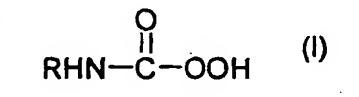
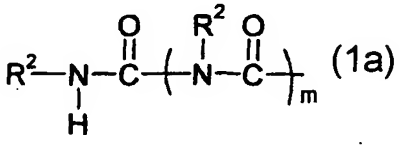


(I)



(1a)

(57) Abstract: The invention provides a method of treatment of a material, comprising contacting said material with a percarbamic acid and/or diacyl percarbamate. Preferably the percarbamic acid has formula (I), where R represents an optionally substituted alkyl, aryl, heteroaryl, cycloalkyl or non-aromatic heterocyclic group, a hydrogen atom, or a group having formula (1a), where each R^2 independently represents a hydrogen atom or an alkyl group; and m = 0 to 30. The method provides effective bleaching agents and or sterilizing agents and or bacteriocidal agents over a wide range of pH and temperatures, for a wide range of applications. Compositions comprise formula (II), whereby R is H or alkyl and L is a moiety displaced by -OOH, and hydrogen peroxide or per hydroxy anion or a precursor therefor.

USE OF PERCARBAMIC ACIDS AND DIACYL PERCARBAMATES AND PRECURSORS THEREFOR

The present invention relates to the preparation and application of percarbamic acids and diacyl precarbamates, in particular to their use in bleaching, sterilisation and purification processes. The invention further relates to certain novel precursors for such acids.

Many bleaches are based on hydrogen peroxide chemistry. Convenient solid carriers of hydrogen peroxide favoured by the laundry industry include sodium percarbonate or perborate, these compounds reacting immediately with water to give free hydrogen peroxide. Hydrogen peroxide functions as an excellent bleach at temperatures greater than 60°C and at pH greater than 10. In order to facilitate low temperature bleaching under normal household washing temperatures of less than 60°C bleach activators are used. Usually bleach activators form the reactive bleach, commonly peracetic acid, by reaction of O-acetyl or N-acetyl species with alkaline hydrogen peroxide.

Examples of bleach activators commonly used in household laundry operations include N,N,N',N'-tetraacetylethylenediamine (TAED), sodium nonanoyloxybenzene-4-sulphonate (SNOBS), glucose-pentaacetate (GPA), di-N-acetyldimethylglyoxin (ADMG) and 1-phenyl-3-acetylhydantoin (PAH). Of the examples listed TAED, which forms peracetic acid, has had the most impact, followed by SNOBS, which forms pernonanoic acid. Such compounds are exemplified in GB 836988, GB 907356, EP 98129, US 2,898,181, US 3,163,606 and EP 120591.

A disadvantage of these compounds is that they do not work effectively at temperatures lower than about 40°C or at acidic and neutral pH.

Recent research has described the use of peramidic acid ($NH_2-(C=NH)OOH$), formed from the reaction of cyanamides, dicyanamides and their acid salts with hydrogen peroxide, for laundry bleaching. Examples are disclosed in US 4,086,177, US 3,756,774 and EP 819673. In each of these examples the use of peramidic acid as the

bleaching agent enables a pH of between 7.5-13 and temperatures of 20-60°C to be used for laundry washing. However in each case the highest activity is still obtained at pH 9-13 and temperatures of 40°-80°.

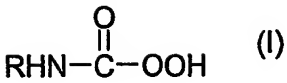
Furthermore cyanamides, dicyanamides and their acid salts are potentially highly toxic, and must therefore be thoroughly rinsed from laundry washed using these compounds as bleach activators.

In JP 9-87685 an aqueous alkaline solution of alkali metal or ammonium cyanate salts, in combination with hydrogen peroxide, is disclosed for use in bleaching/deodorising sports shoes. The optimum pH for the process is 9-11, similar to the other bleaching processes described above. There is no mention of the mechanism of bleaching/deodorising.

EP 543175 discloses the use of cyanate salts and alkaline hydrogen peroxide solutions at pH > 10 for the bleaching of paper pulp. However the disclosure suggests only a small improvement of whiteness.

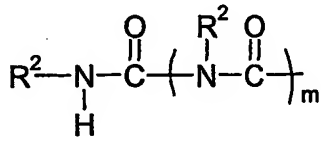
Surprisingly it has been found that percarbamic acids, including percarbamic acid itself and N-substituted percarbamic acids, are effective bleaching agents and/or sterilising and/or bactericidal agents over a wide range of pH and temperatures, and are suitable for a wide range of applications. When the percarbamic acid is formed it is believed that it may be accompanied by the part production of a corresponding diacyl precarbamate.

Accordingly, the present invention provides a method of treatment of a material, comprising contacting said material with a percarbamic acid and/or diacyl percarbamate, preferably in aqueous solution. Preferably the material as contacted with a percarbamic acid. Percarbamic acids and suitable N-substituted percarbamic acids include compounds of general formula



(I)

where R represents an optionally substituted alkyl, aryl, heteroaryl, cycloalkyl or non-aromatic heterocyclic group, a hydrogen atom, a group having the formula



(1a)

where each R^2 independently represents a hydrogen atom or an alkyl group; and m = 0 to 30, preferably 0 to 10, most preferably 0 to 5.

Suitably when R is a group having the formula (1a), each R^2 is identical. Most suitably when R is a group having the formula (1a) each R^2 is a hydrogen atom.

Most preferably R represents an alkyl group or, especially, a hydrogen atom.

We make no claim to methods described in JP 9-87685 or EP 543175. Thus, in the event that the methods described in those documents are shown to make percarbamic acids in situ, we may disclaim a) methods of treating sports shoes, employing hydrogen peroxide or peroxidate and an alkali metal or ammonium cyanate at concentration 0.1-30% w/w on treatment solution at a pH in the range 7 to 13; and b) methods of bleaching paper pulp which employ alkali metal cyanates and hydrogen peroxide at pH>10. Alternatively we may in that event claim our method as being for treatment of materials other than sports shoes and paper pulp.

Suitable diacyl percarbamates include compounds having the formula

R-NH-CO-O-O-CO-NH-R

wherein R is as defined above.

The method of treatment is preferably carried out in the pH range 3 to 11, more preferably 4 to 9 and most preferably 5 to 8.

The method of treatment is preferably carried out at a temperature in the range 0°C to 95°C, more preferably 0°C to 70°C, and most preferably 20°C to 40°C.

Materials to be treated may be organic fibres including cellulose, lignin and hair, inorganic fibres, textile materials including cotton, wool and synthetic textiles, metal surfaces, wood surfaces, ceramic surfaces, plastics surfaces, and liquids, especially aqueous liquids.

The method of treatment is preferably bleaching, for example hair bleaching, textile bleaching, including household laundry and industrial textile bleaching, dye bleaching for both solutions and dyed surfaces, and pulp and paper bleaching.

Alternatively the method of treatment may be sterilisation of surfaces or contaminated water/aqueous solutions, including waste water streams containing dyestuffs and humic components.

A preferred method of the present invention is the bleaching of clothes, especially during washing thereof. In such methods the aqueous solution also contains detergency agents.

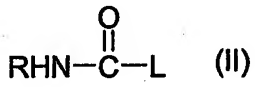
Another preferred method is bleaching of human hair.

Preferably the percarbamic acid and/or diacyl percarbamate is generated in situ. By in situ, we mean that it is generated during or shortly before the method of treatment.

Compounds of general formula (I) in which R represents a hydrogen atom may be prepared, suitably in situ, by the admixture in an aqueous composition of an alkali metal or ammonium cyanate and hydrogen peroxide (or the perhydroxy anion). The reaction to produce the compound of formula (I) is believed to proceed via isocyanic acid HN=C=O.

Compounds of formula (I) in which R represents a hydrogen atom may also be prepared, suitably in situ, by the admixture in an aqueous composition of formamide and hydrogen peroxide (or the perhydroxy anion). Again, the reaction is believed to proceed via isocyanic acid.

A preferred method of generating, preferably in situ, compounds of general formula (I) in which R is a hydrogen atom or an alkyl group comprises reacting a carbamate compound of the general formula



(II)

with hydrogen peroxide (or the perhydroxy anion) where R is as defined above and L is a moiety displaced by the anion

^{-}OOH

The preferred temperature and pH conditions for these three methods are the same as the preferred conditions set out above for the method of treatment.

Preferably L is selected from a phosphonate, phosphinate, thiourea or quaternary ammonium group; or from groups of the formula $-SO_3M$ where M represents a hydrogen atom, or an alkali metal atom, or an ammonium group; or from groups of the formula

$$-XR^3 \text{ or } -Y(R^3)_2$$

where X represents an oxygen or sulphur atom, Y represents a nitrogen atom, and R^3 is selected from hydrogen, optionally substituted alkyl, optionally substituted aryl, optionally substituted amino, cyano, hydroxyl and optionally substituted alkylcarbonyl groups wherein when L is $-Y(R^3)_2$ each R^3 group may be the same or different and is independently selected from the above list, or the groups R^3 and Y may together represent an optionally substituted heteroaryl or non-aromatic heterocyclic group.

Suitable substituents of an aryl or heteroaryl group include halogen, especially fluorine, chlorine and bromine atoms, and nitro, cyano, hydroxyl, alkyl, haloalkyl, haloalkoxy, alkoxyalkyl, aryloxy, alkoxy, alkoxyalkoxy, amino, mono and di-alkylamino, aminoalkyl, mono- and di-alkylaminoalkyl, amido, mono- and di-alkylamido groups and groups of formula - SO_3M or -COOM where M is as defined above. An especially preferred substituent of an aryl group is $-SO_3M$.

Any substituted aryl or heteroaryl group may suitably be substituted by one to three substituents, preferably by one substituent.

Preferred substituents of an alkyl group or of an alkyl moiety within a larger group or of a cycloalkyl or non-aromatic heterocyclic group include halogen, especially fluorine, chlorine or bromine atoms, and nitro, cyano, amidothio ($-S-CONH_2$), amidoamino ($-NH-CONH_2$), hydroxyl, alkoxy, haloalkoxy, -COOM, alkoxycarbonyl, amino and mono- and di-alkylamino and $-SO_3M$ groups, where M is as defined above.

Preferred substituents of an amino group (including of a larger group such as amido) include alkyl, cyano, hydroxyl, alkoxy, amino, amido, thioamido ($-CSNH_2$), aminosaccharide, polyaminosaccharide groups (for example glucosamino and polyglucosamino groups). Preferably an amino group is unsubstituted or mono-substituted, or disubstituted by two alkyl, especially methyl, groups.

Preferred heteroaryl or non-aromatic heterocyclic groups contain 1-3 hetero ring atoms selected from oxygen, sulphur or nitrogen. Preferred groups have at least one ring nitrogen atom. Preferred heteroaryl and non-aromatic heterocyclic groups include

pyrazine and pyridine groups which are unsubstituted or substituted by a single group selected from –COOM and –$CONH_2$, where M is as defined above; piperidine and morpholine groups which are unsubstituted or substituted by a single C_{1-4} alkyl group; and bicyclic non-aromatic heterocycles containing one or two nitrogen atoms, for example azabicyclooctane and diazabicyclooctane.

A preferred sub-class of groups L is those of formula - SO_3M where M is as defined above.

A preferred sub-class of groups L is those of formula -SX where X represents a cyano group, SO_3M (where M is defined above) or an optionally substituted C_{1-6} alkyl group (preferably unsubstituted or substituted by one to three substituents independently selected from -COOM, -SO_3M, hydroxyl, amidothio, optionally substituted amino (preferably NH_2 or –NH-$CONH_2$), optionally substituted alkoxy (preferably unsubstituted), optionally substituted amido (preferably –$CONH_2$) and –COOY, where M is as defined above and Y is an optionally substituted (preferably unsubstituted) alkyl group).

Especially preferred groups L are –SCN and –SO_3M. In relation to any of the foregoing definitions, preferably M represents hydrogen or an alkali metal atom; and especially hydrogen or sodium.

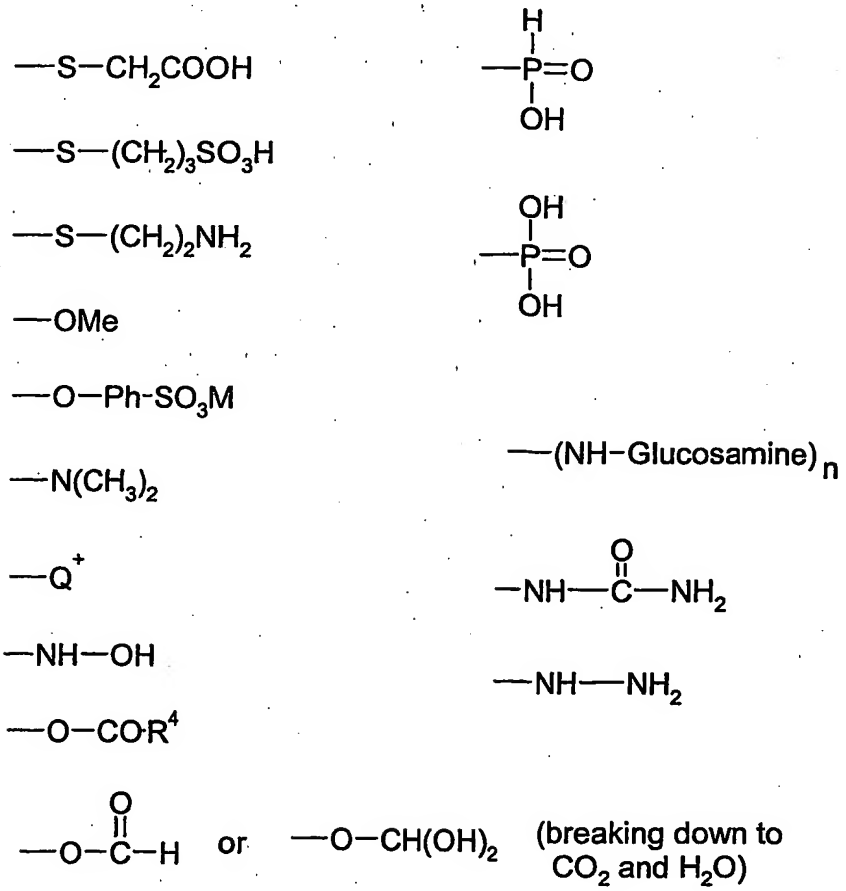
A noteworthy sub-class of groups L is those of formula -OX' where X' represents an optionally substituted (preferably unsubstituted) alkyl group, an optionally substituted (preferably unsubstituted) aryl group or an optionally substituted (preferably unsubstituted) alkylcarbonyl group, or a group –CHO or –OCN. A preferred group L of formula -OX' is -O-PhSO_3M where M is defined above.

A noteworthy sub-class of groups L is those of formula -NX" X'" where X" and X'" may both be alkyl groups or X" may be a hydrogen atom and X'" may be a cyano, alkyl, hydroxyl, amido, amino, aminosaccharide or polyaminosaccharide group.

A noteworthy sub-class of groups L is those of formula -P(=O)R'R" where R' represents hydroxy and R" represents hydrogen or hydroxy or amido.

A noteworthy sub-class Q^+ of groups L is those connected to the C=O group by an N^+ atom, the group Q being a quaternary ammonium moiety formed from a tertiary amine, or a heteroaryl or non-aromatic heterocyclic group as detailed above.

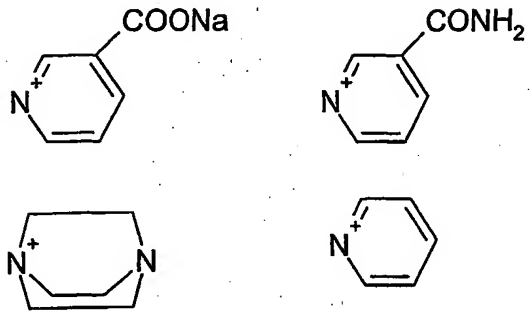
Examples of suitable groups L include:

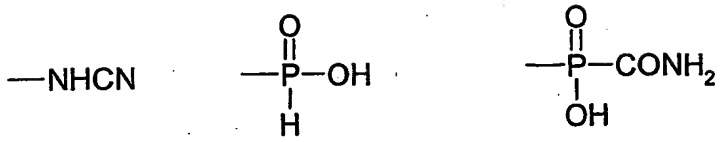


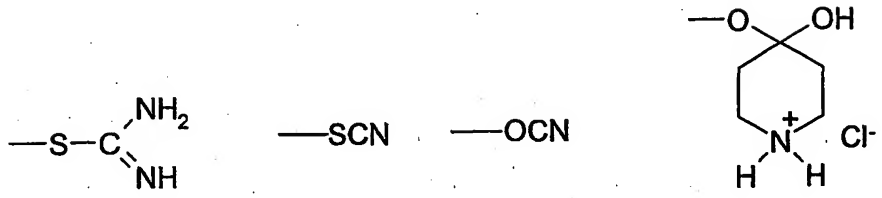
where R^4 is an alkyl group or a hydrogen atom

and, especially

SO_3M (especially SO_3H and SO_3Na)







It should be noted that suitable compounds NHR-CO-L include compounds which may have more than one group NHR-CO-, and so many offer more than one point of attack to the peroxyanion. One example of compound of this type is biuret.

Compounds of formula (II) in which R represents hydrogen may be prepared by a reaction employing an alkali metal or ammonium cyanate and a compound HL where L is as defined above. An alkali metal cyanate, notably sodium cyanate, is preferred. The reaction is believed to proceed via isocyanic acid HN=C=O. The resulting compounds (II) may be isolated but if it is wished they may be contacted with hydrogen peroxide, or the perhydroxy anion, in situ to effect the treatment method.

Preferably the process employing an alkali metal or ammonium cyanate and a compound of formula HL is performed in the presence of a solvent, more preferably in aqueous solution. Suitably the pH of the reaction mixture is maintained between 2 and 10, most preferably between 4 and 8. The pH needed will, however, depend on the nature of L.

Where L is a sulphur-containing leaving group the pH is preferably maintained between 4 and 5 for the duration of the reaction.

Where L is a tertiary amine containing leaving group, such as pyridine, the pH is preferably maintained between 6.5 and 7.5 for the duration of the reaction.

Where L contains an alcoholate residue the pH is preferably maintained between 7 and 8 for the duration of the reaction.

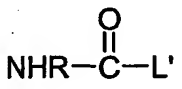
Preferably the reaction is carried out at a temperature between 0°C and 100°C, more preferably between 10°C and 50°C, and most preferably at ambient temperature.

Compounds of formula (II) in which R is not hydrogen may be prepared by reacting an organic isocyanate R-N=C=O with a selected compound HL in the presence of an organic solvent, where L is as defined above. The N-substituted carbamate compounds (II) may be isolated but if it is wished they may be contacted with hydrogen peroxide, or the perhydroxy anion in situ to effect the treatment method. In such cases an organic solvent miscible with water is selected, suitable solvents including isopropanol, acetone, dimethyl formamide and dimethyl sulphoxide.

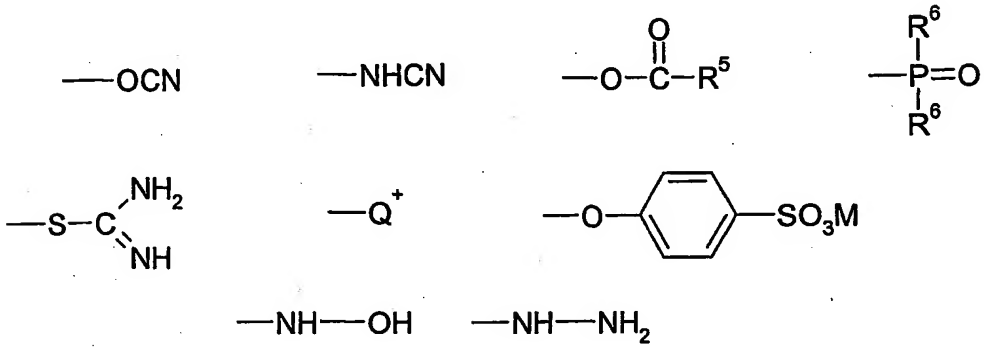
In accordance with a further aspect of the invention there is provided a washing or bleaching or sterilizing or bactericidal composition comprising a compound of formula (II) and hydrogen peroxide or the perhydroxy anion or a precursor therefor. The composition may include a solid concentrate or a liquid concentrate. The composition may when intended for washing or bleaching contain detergent components. A preferred composition comprises a solid, preferably granular, clothes washing

composition, comprising a detergent, a compound of formula (II) and a compound which generates perhydroxy anions in water.

Certain compounds of formula (I) are believed to be novel and accordingly constitute a further aspect of the invention. In this aspect, the invention provides compounds of formula



where R is as defined above (but is preferably hydrogen)
where L' represents a group selected from the following:



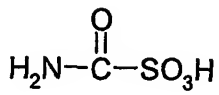
and where R^5 is an optionally substituted alkyl group and each group R^6 is selected independently from H, OH and $CONH_2$, and Q^+ is as defined above.

Such compounds may be prepared as described above, and such methods applied for the preparation of novel compounds constitutes a further aspect of the present invention.

The following examples are used to illustrate the invention. The identity of each of the activators whose preparation was described was confirmed for their IR spectra using a Perkin Elmer 1725 Infrared Fourier Transform Spectrometer, and by microanalysis. Chemicals were obtained from Aldrich unless stated otherwise. Hydrogen peroxide used was 27.5% (w/w) grade; sodium cyanate used was 96% grade.

Example 1

Preparation of Activator 1 (ASP 1)



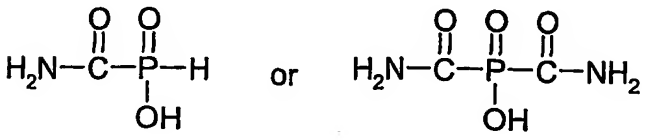
[ASP1]

Sodium cyanate (5g, 0.077 mol) was dissolved in water (50 ml) and stirred for 5 minutes at room temperature; sodium bisulphite (8g, 0.077 mol) was added to this solution. After the sodium bisulphite dissolved, the pH was adjusted pH to 5 using hydrochloric acid (1 M). The reaction was carried out at room temperature, the pH being maintained at 5.0 ~ 5.5. by the addition of hydrochloric acid. When the pH of the solution became stable, the reaction was stopped. The product was precipitated by the addition of 200 ml of ethanol to the reaction solution; the solid was filtered off and dried in ambient air.

An alternative effective preparation was to dissolve sodium metabisulphite (4g, 0.077 mol) in water 5 ml and then to quickly add sodium cyanate (5g, 0.077 mol) maintaining the pH at 4.5 (acetic acid addition) at room temperature. After 10 minutes the product was precipitated using ethanol as above.

Example 2

Preparation of Activator 2 (ASP 2 and 2A)



[ASP2] [ASP2A]

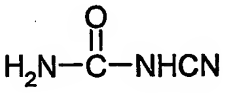
Sodium cyanate (5g, 0.077 mol) was dissolved in water (50 ml) and stirred for 5 minutes; then the pH of the cyanate solution was adjusted to 5 using hydrochloric acid (1 M); Hypophosphorous acid (5g, 50% (w/w) solution, 0.0038 mol) was dissolved in water (20 ml) and gradually added to the stirred cyanate solution over 1 hour; the pH

was maintained at 5. After the addition of hypophosphorous acid, the reaction was continued at room temperature until the pH became stable; the reaction was then stopped. During the reaction, a solid product precipitated; when the reaction finished, this solid was filtered off and dried in ambient air.

A double substitution reaction can occur to give a mixture of products (ASP 2 and ASP 2A); more quantitative yields of ASP 2A can be achieved by giving a larger amount of sodium cyanate. In this example ASP 2A is the predominant product.

Example 3

Preparation of Activator 3 (ASP 3)



[ASP3]

Sodium cyanate (5g, 0.077 mol) was dissolved in water (50 ml) and stirred for 5 minutes at room temperature; then the pH of the cyanate solution was adjusted to 5 using hydrochloric acid (1 M). Cyanamide (3.2g, 0.077 mol) solid was gradually added to the stirred cyanate solution over 1.5 hour, the pH being maintained at 5. After the addition of cyanamide, the reaction was continued at room temperature and at pH 5 ~ 5.5. When the pH of the solution became stable, the reaction was stopped. During the reaction a solid product precipitated; when the reaction finished, this solid was filtered off and dried in ambient air.

Example 4

Tea-stained cotton fabric bleaching using bleach activators ASP 1 to ASP 3 from Examples 1 to 3.

Tea-stained cotton fabric was prepared by the following method:

Three small tea bags of British-style "brown" tea were placed in 1000 ml of water and boiled for 15 minutes. A plain weave cotton fabric was impregnated by adding this

solution (wet pick-up 100%) and this fabric was allowed to dry in ambient air. This fabric was then left in a laboratory oven for 60 minutes at 60°C.

The bleach solution was made up as follows:

Hydrogen peroxide (100%) 5g/l

Bleach activator 3g/l

pH buffer

Goods to liquor ratio 1:10

pH buffer used was: pH 5 or 7 – sodium dihydrogen phosphate (0.1M) and sodium hydroxide (0.1M)

pH 10 – sodium carbonate

Tea stained fabric, as described above, and bleach solution were put in to a 100cm^3 sealed stainless steel dyepot and placed in a laboratory dyeing machine (Rotadyer). The bleaching process was carried out for 45 minutes at the selected temperature. After bleaching, the fabric was washed thoroughly in tap water and dried in ambient air. The CIE whiteness values of the tea stained starting fabric was measured, and found to be – 34.4.

Table 1 CIE whiteness values of fabric bleached at pH 5 at different temperatures

	CIE Whiteness		
Bleaching Species	20°C	50°C	95°C
H_2O_2	24.5	35.5	62.2
H_2O_2 + ASP 1	42.8	44.1	77.0
H_2O_2 + ASP 2/2A	23.0	34.9	63.7
H_2O_2 + ASP 3	21.2	41.4	65.2

Table 2 CIE whiteness values of fabric bleached at pH 7 at different temperatures

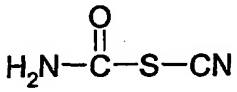
	CIE Whiteness		
Bleaching Species	20°C	50°C	95°C
H_2O_2	39.1	43.1	75.9
H_2O_2 + ASP 1	64.2	65.7	84.8
H_2O_2 + ASP 2/2A	37.6	47.6	74.4
H_2O_2 + ASP 3	38.3	52.9	73.0

Table 3 CIE whiteness values of fabric bleached at pH 10 at different temperatures

	CIE Whiteness		
Bleaching Species	20°C	50°C	95°C
H_2O_2	61.8	60.7	77.8
H_2O_2 + ASP 1	72.0	74.0	80.6
H_2O_2 + ASP 2/2A	58.1	65.7	85.1
H_2O_2 + ASP 3	57.6	74.4	85.1

Example 5

Preparation of Activator 5 (ASP 7)



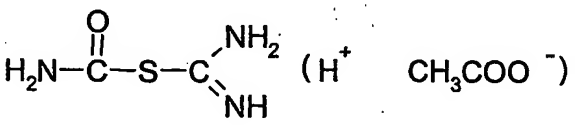
[ASP7]

Sodium cyanate (5g, 0.077 ml) was dissolved in water (50 ml) and stirred for 5 minutes at room temperature; sodium thiocyanate (8.1g, 0.1 mol) was added to this solution. After the sodium thiocyanate dissolved, the pH was adjusted to 5 using acetic acid. The reaction was carried out at room temperature, the pH being maintained at 5.0 ~ 5.5 by the addition of acetic acid; when the pH of the solution became stable, the

reaction was stopped. The product was precipitated by the addition of 300 ml of ethanol to the reaction mixture. The solid was filtered off and dried in ambient air.

Example 6

Preparation of Activator 6 (ASP 8)

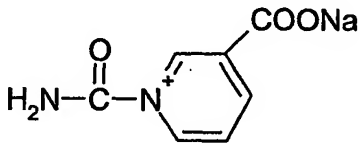


[ASP8]

Sodium cyanate (5g, 0.077 ml) was dissolved in water (70 ml) and stirred for 5 minutes; then the pH of the cyanate solution was adjusted to 5 using acetic acid. Thiourea solid (7.6g, 0.1 mol) was added to the stirred cyanate solution over 1 hour; the pH was maintained at 5 ~ 5.5. After the addition of thiourea, the reaction was continued at room temperature until the pH became stable; the reaction was then stopped. The product (an isothiouronium salt) was precipitated by the addition of 300 ml of ethanol to the reaction mixture; the solid was filtered off and dried in ambient air.

Example 7

Preparation of Activator 7 (ASP 9)



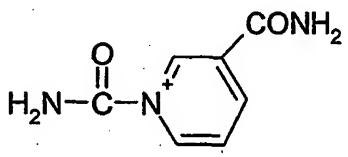
[ASP9]

Sodium cyanate (5g, 0.077 mol) was dissolved in water (50 ml) and stirred for 5 minutes at room temperature; nicotinic acid solid (9.5g, 0.077 mol) was gradually added to the stirred cyanate solution to keep pH maintained at 5 - 5.5 (no other acid was needed). After the addition of nicotinic acid, the reaction was continued at room temperature and at pH 5 - 5.5. When the pH of the solution became stable, the reaction

was stopped. The product was precipitated by the addition of 400 ml of acetone to the mixture reaction; the solid was filtered off and dried in ambient air.

Example 8

Preparation of Activator 8 (ASP 10)

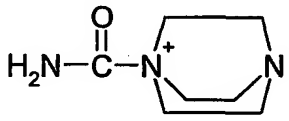


[ASP10]

Sodium cyanate (5g, 0.077 mol) was dissolved in water (50 ml) and stirred for 5 minutes at room temperature; then the pH of the cyanate solution was adjusted to 5 using acetic acid. Nicotinic amide solid (12.2g, 0.1 mol) was gradually added to the stirred cyanate solution over 1.5 hour; the pH was maintained at 5. After the addition of nicotinic amide, the reaction was continued at room temperature and at pH 5 ~ 5.5. When the pH became stable, the reaction was stopped. The product was precipitated by the addition of acetone (350 ml) to the reaction mixture; the solid was filtered off and dried in ambient air.

Example 9

Preparation of Activator 9 (ASP11)



[ASP11]

Sodium cyanate (5g, 0.077 mol) was dissolved in water (50 ml) and stirred for 5 minutes at room temperature; then the pH of the cyanate solution was adjusted to 5 using acetic acid. Solid diazabicyclooctane (DABCO) (8.6g, 0.0077 mol) was gradually added to the stirred cyanate solution over 1 hour; the pH was maintained at

5. After the addition of DABCO, the reaction was continued at room temperature and at pH 5-5.5. When the pH became stable, the reaction was stopped. The product was precipitated by the addition of acetone (350 ml) to the reaction mixture; the solid was filtered off and dried in ambient air.

Example 10

Tea stained cotton fabric bleaching using bleach activators (ASP 7 to ASP 11) of Examples 5 to 9.

Tea-stained cotton fabric, the bleach method and conditions, were the same as those described in Example 4; but the CIE whiteness value of the tea-stained starting fabric was –52.4.

Table 4 CIE whiteness values of fabric bleached at pH 5 at different temperatures

Bleaching Species	CIE Whiteness		
	20°C	50°C	95°C
H_2O_2	-27.3	-2.3	33.9
H_2O_2 + ASP 7	-22.4	42.8	65.8
H_2O_2 + ASP 8	-25.3	-4.8	52.1
H_2O_2 + ASP 9	-26.3	-3.6	47.0
H_2O_2 + ASP 10	-29.8	-5.5	31.5
H_2O_2 + ASP 11	-27.6	-8.5	35.5

Table 5 CIE whiteness values of fabric bleached at pH7 at different temperatures

Bleaching Species	CIE Whiteness		
	20°C	50°C	95°C
H_2O_2	-0.3	5.3	67.5
H_2O_2 + ASP 7	39.3	55.8	81.0
H_2O_2 + ASP 8	7.7	40.7	81.2
H_2O_2 + ASP 9	8.0	31.9	75.7
H_2O_2 + ASP 10	0.2	8.4	69.3
H_2O_2 + ASP 11	1.6	11.2	71.9

Table 6 CIE whiteness values of fabric bleached at pH 10 at different temperatures

Bleaching Species	CIE Whiteness		
	20°C	50°C	95°C
H_2O_2	23.1	54.4	70.6
H_2O_2+ ASP 7	40.4	68.6	80.5
H_2O_2 + ASP 8	31.4	62.1	83.5
H_2O_2 + ASP 9	23.8	68.9	81.3
H_2O_2 + ASP 10	21.7	60.2	76.9
H_2O_2 + ASP 11	21.2	64.5	80.1

Example 11

Raman analysis of the reaction between hydrogen peroxide and carbamate (ASP 1 from Example 1).

Raman analysis of the reaction between ASP 1 (10% w/w) and hydrogen peroxide (10% w/w) at pH 6 showed percarbamic acid species formation, as characterised by absorption bands at 896cm^{-1}, 876cm^{-1}, and 853cm^{-1} (using secondary derivative analysis of the spectrum).

Example 12

Tea-stained cotton fabric bleaching using sodium cyanate and TAED (N, N, N', N' – tetraacetylethylenediamine ex Fluka Chemical, 95% grade).

Tea-stained cotton fabric, bleach solutions, conditions and the method of bleaching were the same as described in Example 4, but the CIE whiteness of the tea-stained starting fabric in these experiments was –30.8.

Bleach activators used were sodium cyanate and TAED.

Table 7 CIE whiteness values of fabric bleached at pH 5 at different temperatures

Bleaching species	20°C	50°C	95°C
H_2O_2	0.6	23.1	60.8
$NaOCN + H_2O_2$	24.8	67.6	83.4
$TAED + H_2O_2$	5.8	46.6	76.6

Table 8 CIE whiteness values of fabric bleached at pH 7 at different temperatures

Bleaching species	20°C	50°C	95°C
H_2O_2	13.6	36.6	81.0
$NaOCN + H_2O_2$	51.4	78.2	84.1
$TAED + H_2O_2$	49.8	76.6	79.8

Table 9 CIE whiteness values fabric bleached at pH 10 at different temperatures

Bleaching species	20°C	50°C	95°C
H_2O_2	33.3	62.9	78.2
$NaOCN + H_2O_2$	55.4	72.2	82.7
$TAED + H_2O_2$	47.0	71.9	71.6

Example 13

Raman analysis of the reaction employing sodium cyanate and hydrogen peroxide.

Raman analysis of the reaction employing sodium cyanate (10% w/w) and hydrogen peroxide (10% w/w) at pH 8 showed percarbamic acid species formation as characterised by absorption bands at 896 cm^{-1}, 876 cm^{-1} and 853 cm^{-1} (second derivative spectra).

Example 14

Tea-stained cotton fabric bleaching using sodium cyanate, and TAED.

Tea-stained cotton fabric, bleach solutions, conditions and the method of bleaching were the same as described in Example 4, except the amount of bleach activator used (sodium cyanate, or TAED) was 0.1g/l as opposed to 3g/l in Example 4.

Table 10 CIE whiteness values of fabric bleached at pH 7 or 10 at 50°C.

Bleaching species	pH 7	pH 10
H_2O_2	38.7	62.9
H_2O_2 + NaOCN	74.5	66.6
H_2O_2 + TAED	65.3	63.8

Example 15

Tea-stained cotton fabric using formamide

Tea-stained cotton fabric, the bleach method and conditions, were the same as those described in Example 4.

Table 11 CIE whiteness values of fabric bleached at 95^{0}C at different pH values

Bleaching Species	CIE Whiteness	
	pH=7	pH=10
H_2O_2	69.6	79.5
H_2O_2 + Formamide	80.6	73.8

Table 12 CIE whiteness values of fabric bleached at 50^{0}C at different pH values

Bleaching Species	CIE Whiteness		
	pH=5	pH=7	pH=10
H_2O_2	35.6	43.6	60.3
H_2O_2 + Formamide	35.8	48.5	61.6

It will be seen from the above examples that certain bleach activators give optimal performance at particular pH and temperature conditions. Accordingly appropriate activators may be selected, having regard to the bleaching processes to be carried out. For example wool is generally bleached under near-neutral and mild conditions whereas cotton is generally bleached under alkaline high temperature conditions.

Example 16

Bleaching of dye solutions

Dye solution was prepared by dissolving Remazol Black B (Dystar) (0.1g) in water (1000 ml). For each sample 20 ml of the dye solution was used.

The bleaching solution was prepared as follows:

Dye solution 20 ml

Hydrogen peroxide 4g

Bleach activator 2g/l

pH 3, 7 or 10

Total volume 25 ml

pH 3 was obtained with acetic acid; pH 7 was obtained with sodium dihydrogen phosphate (0.1M) and sodium hydroxide (0.1M); pH 10 was obtained using sodium carbonate.

The bleaching solutions were left at 20°C, and the absorbance values were measured after 3 hours and 24 hours using UV/visible spectrophotometry at 600 nm. The degree of dye removal or bleaching (R%) was calculated using the following equation:

$$\% R = 1 - (A_2/A_1) \times 100$$

where A_1 and A_2 are the absorbance values of the solution before and after bleaching.

The results are shown in the following tables.

Table 13 The degree of dye removal (%R) at pH 3 and 20°C

Bleaching Species	3 hours		24 hours	
	Absorbance	%R	Absorbance	%R
H_2O_2	2.243	3.3	2.122	8.5
$NaOCN + H_2O_2$	1.853	20.1	1.684	27.4
$TAED + H_2O_2$	2.197	5.3	2.187	5.7
Absorbance before bleach	2.320			

Table 14 The degree of dye removal at pH 7 and 20°C

Bleaching Species	3 hours		24 hours	
	Absorbance	%R	Absorbance	%R
H_2O_2	2.257	2.7	2.155	7.1
$NaOCN + H_2O_2$	0.892	61.6	0.585	74.8
$TAED + H_2O_2$	1.695	27.0	1.318	43.2
Absorbance before bleach	2.320			

Table 15 The degree of dye removal at pH 10 and 20°C

Bleaching Species	3 hours		24 hours	
	Absorbance	%R	Absorbance	%R
H_2O_2	2.057	11.3	1.625	24.8
$NaOCN + H_2O_2$	1.439	38.0	0.891	61.6
$TAED + H_2O_2$	2.320	0.0	1.077	53.6
Absorbance before bleach	2.320			

Example 17

Bleaching of human black hair

The bleach solution was prepared as follows:

Hydrogen peroxide (100%) 1-3% W/W

Sodium cyanate 3-6% W/W

Ethylenediaminetetraacetic acid disodium salt, 2-3% V/V

D-gluconic acid 3% W/W

Balance water

pH 5

The human black hair tress was impregnated with this solution at 35°C for 15-30 minutes, washed with tap water to remove residual bleach species and allowed to dry in air. The black hair was found to be bleached to a different blonde shade depending on the bleaching species concentration and bleach. If sodium cyanate was omitted, no bleaching effect was detected.

Example 18

Cultures of *E. Coli* in Ringer's saline were exposed to various conditions for 45 minutes at 37°C. These were then serially diluted (eight 10-fold dilutions) and plated onto nutrient agar (treatments were done in triplicate to ensure reproducibility), and five tests were done overall as shown below. Initial *E. Coli* concentration was approximately 5×10^9/ml and cultures were grown in nutrient broth overnight before being centrifuged and then re-suspended in saline.

A. *E. Coli* control - time zero.

B *E. Coli* control - time 45 minutes

C *E. Coli* plus peroxide at 5g/1 for 45 minutes

D *E. Coli* plus ASP 1 at 3g/1 for 45 minutes

E *E. Coli* plus peroxide of 5g/1 plus ASP 1 (3g/1) for 45 minutes

Plates were observed and counted after 2 days incubation at 37°C

Counts recorded were as follows:-

A 40×10^8 colony forming units ml^{-1}

B 37×10^8 colony forming units ml^{-1}

C 12.9 x 10^8 colony forming units ml^{-1}

D 7.9 x 10^8 colony forming units ml^{-1}

E ~0 colony forming units ml^{-1}

(Results given are the averages of the three experiments and all of the replicates show very close agreement).

A and B were as expected about the same, C showed a moderate reduction (~66%) due to the presence of peroxide. D showed a reduction of about 80% due to ASP 1. E showed no bacterial growth, indicating 100% kill in the 45 minutes treatment period. In should be pointed out that in disinfecting bacteria, reductions in the order 90-99% are small, given the very large numbers which can be present to start with. The decrease in bacteria count in D may be due to toxicity of ASP 1 or possibly to the ASP 1 increasing the toxic effect of endogenously produced peroxide. Clearly the combination of peroxide and ASP 1 is highly effective. The above composition was also an effective bacteriocide against pseudomonas aeruginosa, staphylococcus epidermis and aspergillus niger.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

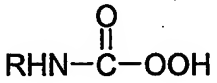
The invention is not restricted to the details of the foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Claims

1. A method of treatment of a material, comprising contacting said material with a percarbamic acid and/or diacyl percarbamate.

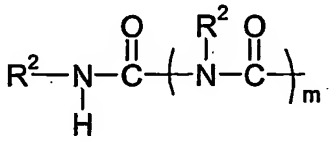
2. A method as claimed in claim 1, wherein the percarbamic acid and/or diacyl percarbamate is in aqueous solution.

3. A method as claimed in claim 1 or 2, wherein the percarbamic acid is a compound of general formula



(I)

where R represents an optionally substituted alkyl, aryl, heteroaryl, cycloalkyl or non-aromatic heterocyclic group, a hydrogen atom, or a group having the formula



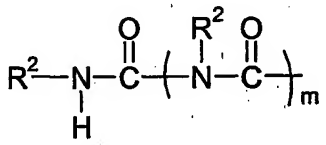
(1a)

where each R^2 independently represents a hydrogen atom or an alkyl group; and m = 0 to 30.

4. A method as claimed in claim 1 or 2, wherein the diacyl percarbamate is a compound having the formula

R-NH-CO-O-O-CO-NH-R

wherein R represents an optionally substituted alkyl, aryl, heteroaryl, cycloalkyl or non-aromatic heterocyclic group, a hydrogen atom, or a group having the formula



(1a)

where each R^2 independently represents a hydrogen atom or an alkyl group; and m = 0 to 30.

5. A method as claimed in any preceding claim, wherein the method of treatment is carried out in the pH range 3 to 11.

6. A method as claimed in any preceding claim, wherein the method of treatment is carried out at a temperature in the range 0°C to 95°C.

7. A method as claimed in any preceding claim, wherein the material to be treated is an organic fibre, such as cellulose, lignin and hair, an inorganic fibre, a textile material such as cotton, wool and synthetic textiles, a metal surface, a wood surface, a ceramic surface, a plastics surface, a liquid, or an aqueous liquid.

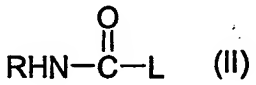
8. A method as claimed in any preceding claim, wherein the method is a method of bleaching.

9. A method as claimed in any of claims 1 to 7, wherein the method is a method of sterilisation of a surface or a contaminated aqueous solution.

10. A method as claimed in any preceding claim, wherein the percarbamic acid and/or diacyl percarbamate is generated in situ.

11. A method as claimed in claim 3, in which R represents a hydrogen atom, wherein the compound of general formula (I) is prepared by the admixture in an aqueous composition, of an alkali metal or ammonium cyanate and hydrogen peroxide or the perhydroxy anion.

12. A method as claimed in claim 3, in which R is a hydrogen atom or an alkyl group, wherein the compound of general formula (I) is generated by reacting a carbamate compound of the general formula



(II)

with hydrogen peroxide or the perhydroxy anion where R is a hydrogen atom or alkyl group and L is a moiety displaced by the anion

^{-}OOH

13. A method as claimed in claim 12, wherein L is selected from a phosphonate, phosphinate, thiourea or quaternary ammonium group; or from groups of the formula - SO_3M where M represents a hydrogen atom, or an alkali metal atom, or an ammonium group; or from groups of the formula

$$- X R^3 \text{ or } - Y (R^3)_2$$

where X represents an oxygen or sulphur atom, Y represents a nitrogen atom, and R^3 is selected from hydrogen, optionally substituted alkyl, optionally substituted aryl, optionally substituted amino, cyano, hydroxyl and optionally substituted alkylcarbonyl groups, wherein when L is $-Y(R^3)_2$ each R^3 group may be the same or different and is independently selected from the above list, or the groups R^3 and Y may together represent an optionally substituted heteroaryl or non-aromatic heterocyclic group.

14. A method as claimed in claim 13, wherein L has the formula –SX where X represents a cyano group, an optionally substituted C_{1-6} alkyl group or SO_3M, where M represents a hydrogen atom, an alkali metal atom, or an ammonium group.

15. A method as claimed in claim 13, wherein L is –OX' where X' represents an optionally substituted alkyl group, an optionally substituted aryl group or an optionally substituted alkylcarbonyl group, or a group –CHO or –OCN.

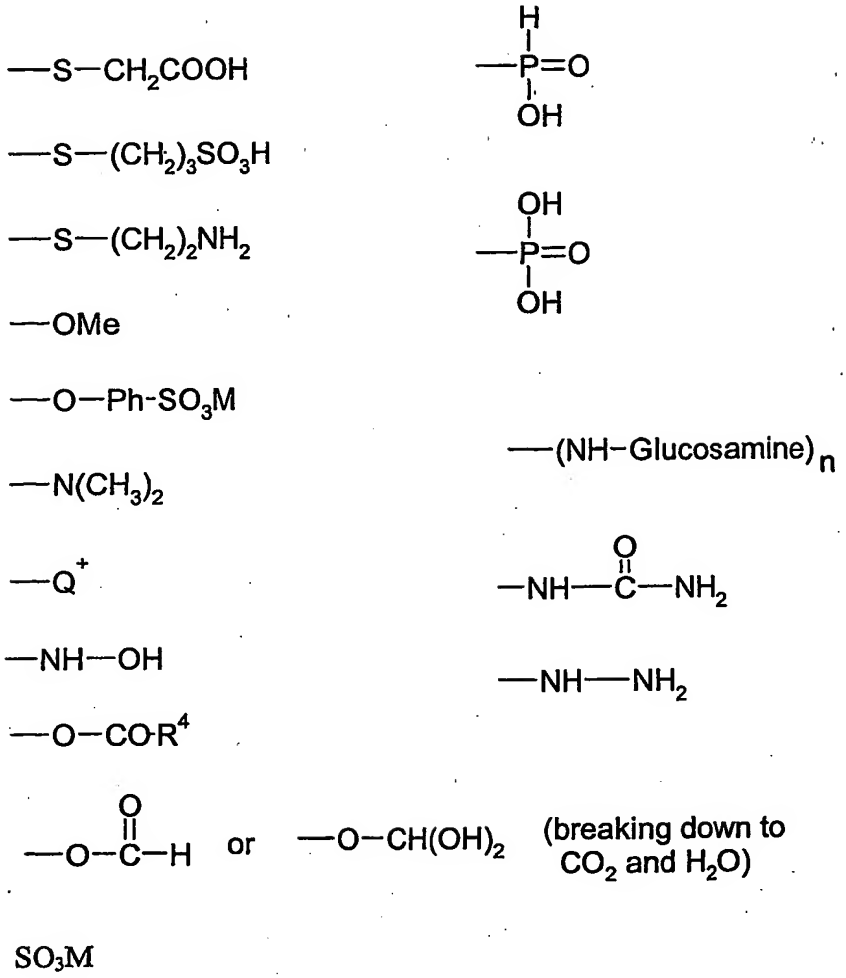
16. A method as claimed in claim 13, wherein L is –O –$PhSO_3M$, where M is a hydrogen atom, an alkali metal atom, or an ammonium group.

17. A method as claimed in claim 13, wherein L is -NX" X"' where X" and X"' may both be alkyl groups or X" may be a hydrogen atom and X"' may be a cyano, alkyl, hydroxyl, amido, amino, aminosaccharide or polyaminosaccharide group.

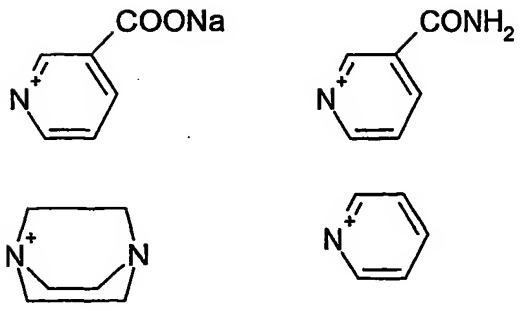
18. A method as claimed in claim 13, wherein L is of formula –P(=O)R'R" where R' represents a hydroxyl group and R" represents hydrogen or hydroxyl group or amido group.

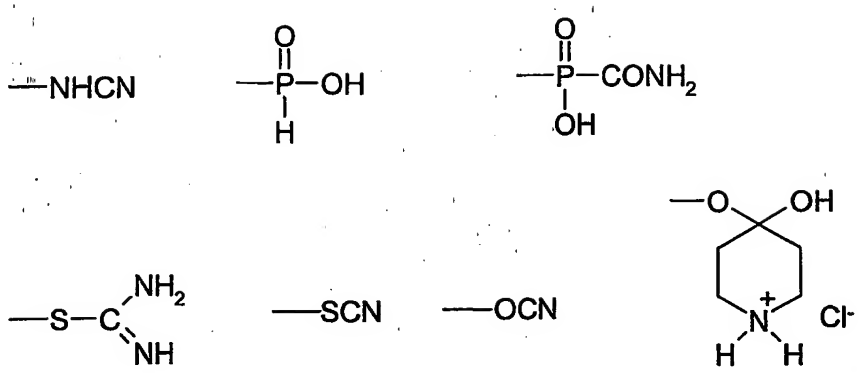
19. A method as claimed in claim 13, wherein L is Q^+ connected to the C=O group by an N^+ atom, the group Q being a quaternary ammonium moiety formed from a tertiary amine, or a heteroaryl or non-aromatic heterocyclic group.

20. A method as claimed in claim 13, where L is a group selected from the following:


—S—CH2COOH
—S—(CH2)3SO3H
—S—(CH2)2NH2
—OMe
—O—Ph-SO3M
—N(CH3)2
—Q+
—NH—OH
—O—CO-R4
—O—C(=O)—H
or
—O—CH(OH)2
(breaking down to CO2 and H2O)
SO3M
—P(H)(=O)—OH
—P(OH)(=O)—OH
—(NH-Glucosamine)n
—NH—C(=O)—NH2
—NH—NH2

5


COONa
CONH2
N+
N+
N+
N+
N



wherein M is a hydrogen atom, an alkali metal, or an ammonium group and where R^4 is an alkyl group or a hydrogen atom.

21. A method as claimed in claim 12, in which R represents hydrogen, wherein the compound of formula (II) is prepared by a reaction employing an alkali metal or an ammonium cyanate and a compound HL where L is a moiety displacable by the perhydroxy anion.

22. A method as claimed in claim 21, wherein the compound of formula (II) is contacted with hydrogen peroxide, or the perhydroxy anion, in situ.

23. A method as claimed in claim 21 and 22, wherein the pH of the reaction mixture is maintained between 2 and 10.

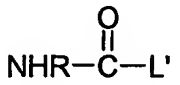
24. A method as claimed in claim 12, in which R is not hydrogen, wherein compounds of formula (II) are prepared by reacting an organic isocyanate R-N=C=O with HL in the presence of an organic solvent, wherein L is a moiety displacable by the perhydroxy anion.

25. A washing or bleaching or sterilizing or bactericidal composition comprising a compound of formula (II) as defined in any of claims 12 to 24 and hydrogen peroxide or the perhydroxy anion or a precursor therefor.

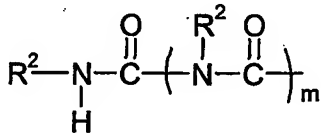
26. A composition as claimed in claim 25, wherein the composition is a solid concentrate or a liquid concentrate.

27. A composition as claimed in claim 25 or 26, wherein the composition is a solid clothes washing composition, comprising a detergent, a compound of formula (II) and a compound which generates perhydroxy anions in water.

28. A compound of formula

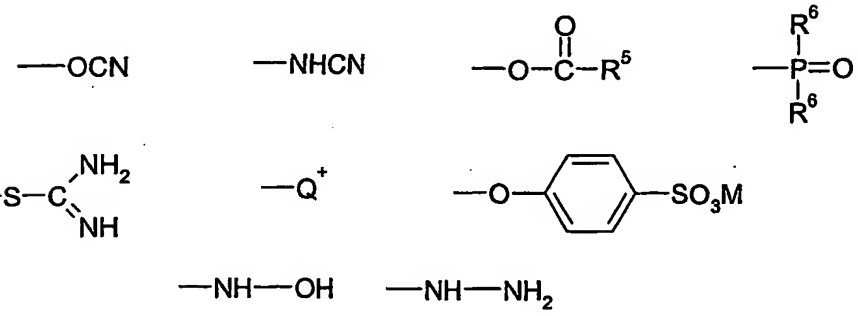


where R represents an optionally substituted alkyl, aryl, heteroaryl, cycloalkyl or non-aromatic heterocyclic group, a hydrogen atom, or a group having the formula



(1a)

where each R^2 independently represents a hydrogen atom or an alkyl group; and m = 0 to 30; and where L' represents a group selected from the following:



wherein R^5 is an optionally substituted alkyl group and each R^6 is selected independently from hydrogen, a hydroxyl group, an amido group and a quaternary ammonium group.

5

INTERNATIONAL SEARCH REPORT

In ional Application No
PCT/GB 01/03656

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/39 D06L3/02 D21C9/16 A61L2/18 C02F1/72
A61K7/135 C07C261/02 A61L2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D D06L D21C A61L C02F A61K C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 28 47 267 A (HENIG HANS) 8 May 1980 (1980-05-08) page 17; claim 18 page 10 ---	1-11
X	DATABASE WPI Section Ch, Week 199723 Derwent Publications Ltd., London, GB; Class A97, AN 1997-255879 XP002184694 & JP 09 087685 A (JOHNSON KK), 31 March 1997 (1997-03-31) cited in the application abstract --- -/---	1-11

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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Date of the actual completion of the international search	Date of mailing of the international search report
4 December 2001	18/12/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Pfannenstein, H

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 0 543 175 A (DEGUSSA) 26 May 1993 (1993-05-26) cited in the application page 2 -page 4 ---	1-11
X	DE 23 64 636 A (DEGUSSA) 10 July 1975 (1975-07-10) claims; examples ---	1-11
X	DATABASE WPI Section Ch, Week 197748 Derwent Publications Ltd., London, GB; Class A35, AN 1977-85474Y XP002184698 & JP 52 124758 A (TOA GOSEI CHEM IND LTD), 20 October 1977 (1977-10-20) abstract ---	1-11
X	CHEMICAL ABSTRACTS, vol. 107, no. 6, 10 August 1987 (1987-08-10) Columbus, Ohio, US; abstract no. 42129, XP002184693 abstract & JP 62 001793 A (KAO) 7 October 1987 (1987-10-07) --- -/--	1-13, 25-27

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 01/03656

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LAPSHIN N M ET AL: "INFRARED SPECTRA OF SOME PERCARBONATES AND PERCARBAMATES" ZURNAL ORGANICESKOJ KHIMII, MAIK NAUKA, MOSCOW, RU, vol. 4, no. 6, 1968, pages 952-954, XP002937056 ISSN: 0514-7492 page 952	1-11
X	BEILSTEIN DATABASE FILE XFIRE, XP002184692 SEE ATTACHED BRNS	28
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Information on patent family members

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